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THE INTERPRETATION OF POLYMER DATA. (U)

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10 Neil S. Berman

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Subject: The Interpretation of Polymer Data

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Abstract: Using a log normal model for molecular weight distribution, drag curves can be predicted which agree with experiments in pipe flow. Working back from pipe flow data, average molecular weights or concentrations can be estimated from drag curves. Illustrations are given for a recent water tunnel test and data in the literature.

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THE INTERPRETATION OF POLYOMETER DATA

Introduction

Drag reduction by dilute polymer solutions is easily illustrated by pressure drop vs. flow rate curves for turbulent flow in a circular pipe. It is desired to compare such tests to experiments in other geometries with polymers of different molecular weight distributions and different solution concentrations. For example in a polymer ocean test the polymer initially is fresh with a certain molecular weight distribution, and as it degrades it may be equivalent (for drag reduction at least) to a fresh solution of a lower concentration. In the analysis in this appendix we first describe the presentation of pipe flow data and then develop a model to relate the curves to concentration and molecular weight distribution.

Presentation of Data

Over the range of Reynolds numbers 10^4 to 10^5 the flow rate for turbulent flow can be related to the shear rate by a power law relationship. In terms of Q in cubic centimeters per second and U_*^2/ν in sec^{-1}

$$Q_{\text{water}} = 0.69D^{2.15} \left[\frac{U_*^2}{\nu} \right]^{0.572} \quad (1)$$

Here D is the pipe diameter and U_*^2/ν equals τ_w/μ equals $(-\Delta p)D/4L\mu$ where ν is the kinematic viscosity, μ , the viscosity, τ_w , the shear stress at the wall, and $-\Delta p/L$, the pressure drop per unit length. The limiting drag reduction asymptote as given by Virk (1967) can also be expressed in a similar form:

$$Q_{\max} = 0.71 D^{2.31} \left[\frac{U_*^2}{\nu} \right]^{0.654} \quad (2)$$

Now when a curve of Q vs. U_*^2/ν is measured using the polyometer described in another section, several different types of behavior are found. These are illustrated on fig. 1. Curve I shows a polymer solution containing sufficient polymers of a high enough molecular weight to exhibit maximum drag reduction at all Reynolds numbers. When the polymer molecular weight is the same as for Curve I but the concentration is too low to reach the maximum drag reduction line, Curve II results. Keep in mind that the polymer solutions we are discussing have a molecular weight distribution and are not of a single molecular weight. The next curve, III, illustrates a solution with lower molecular weight polymers than in Curves I and II but enough concentration to reach maximum drag reduction at a sufficiently high value of shear rate. In this case the curve approximately follows the water turbulent

line up to an "onset" shear stress and then proceeds at a greater slope to the maximum drag reduction line. In reality the deviation from the turbulent water and the intersection with the maximum drag reduction lines are not sharp as shown but very gradual. In almost all cases, however, the curve can be well approximated by a straight line drawn between the water and maximum drag reduction lines. Curve IV shows another such line with not enough experimental data at very high shear rates. This curve would eventually reach the maximum drag reduction line. Finally Curve V represents the curve for the minimum concentration of polymer so that at a shear rate of infinity the maximum drag reduction curve is reached. Other curves beyond this would never reach maximum drag reduction.

Description of Data

Now to describe these curves mathematically we can consider only those of types III, IV, and V. Curve I may of course change to Curve III if a larger size pipe is used in the polyometer (lower transition shear stress). We can define two types of fractions to represent the points between the turbulent water and the maximum drag reduction curves as follows:

$$\Delta_S \equiv \left[\frac{Q_p - Q_w}{Q_M - Q_w} \right] U_*^2 / \nu = \text{Const.} \quad (3)$$

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$$\Delta_R \equiv \left| \frac{f_w - f_p}{f_w - f_M} \right|_{N_{Re} = \text{Const.}} \quad (4)$$

where the subscript p is for polymer, w, for water, and M, for maximum drag reduction, and f is the friction factor. For the polyometer curves

$$\Delta_R = \left| \frac{\left(\frac{U_*^2}{v}\right)_w - \left(\frac{U_*^2}{v}\right)_p}{\left(\frac{U_*^2}{v}\right)_w - \left(\frac{U_*^2}{v}\right)_M} \right|_{Q = \text{Const.}} \quad (5)$$

Figure 2 shows some possible Δ_S and Δ_R locations. About point P we have

$$\Delta_S = \frac{\overline{PB}}{\overline{AB}}$$

$$\Delta_R = \frac{\overline{DP}}{\overline{DC}}$$

where \overline{XY} denotes the number X minus the number Y and not the length or log coordinates. For many water tunnel tests we need a fractional drag reduction to aid in the explanation of the data. For skin friction drag in turbulent flow, when the water would be at point B, the fractional drag reduction for the illustrated polymer solution at the same free stream velocity is $(1-G/B)$. If an experiment

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involves an irrotational flow and the strain rate is the important parameter then the appropriate functional drag reduction for the illustrated polymer for a shear rate on the line APB is $(1-P/D)$.

Log Normal Model

We would like to relate the point P and all points on the line OPT to the molecular weight distribution, concentration, and behavior of polymer in the turbulent flow. Although the molecular weight distribution in the dilute polymer blend is probably complex, we choose a log normal distribution as representative.

Then

$$P(M) = \frac{1}{\sqrt{2\pi}\beta M} e^{-\frac{(\ln M - m)^2}{2\beta^2}} \quad (6)$$

where $\beta^2 = \langle (\ln M - m)^2 \rangle$

$$m = \langle \ln M \rangle$$

$$\langle M \rangle = e^m + \frac{1}{2}\beta^2 \quad (7)$$

and $\langle x \rangle = \int_0^{\infty} \frac{x}{\sqrt{2\pi}\beta M} \exp\left[-\frac{(\ln M - m)^2}{2\beta^2}\right] dM \quad (8)$

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Here $\langle M \rangle$ is the number average molecular weight. Now we assume that the difference between a parameter characteristic of the flow for polymer solutions and that for water alone can be found by summing up all the contributions from all molecular weights above an onset value, M_0 . Let δ be this parameter with subscript p for polymer and w for water. The appropriate property to be summed will be taken as the effective volume, $C [\eta]$ where C is the concentration and $[\eta]$, the intrinsic viscosity.

Then

$$\delta_p - \delta_w \sim \int_{M_0}^{\infty} C [\eta] P(M) dM \quad (9)$$

It is an easy matter to put eq. 9 in terms of the molecular weight alone. The terminal relaxation time, T_1 , can be related to molecular weight and intrinsic viscosity as follows

$$T_1 = \frac{\eta_s [\eta] M}{2RT} \quad (10)$$

where η_s is the solvent viscosity, T, the absolute temperature, R, the gas constant, and $[\eta]$, the intrinsic viscosity. For polyox Merrill finds

$$[\eta] = 1.03 \times 10^{-4} M^{0.78} \quad (11)$$

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in units of deciliters/gram. Then at 25°C for water as the solvent

$$T_1 = 2 \times 10^{-15} M^{1.78}$$

(12)

To relate to the polyometer curve we need the relationship between T_1 and the flow timescale U_*^2/ν . Lumley finds that the condition for ultimate expansion of the polymer molecules in turbulent flow is given by

$$2|\lambda|^2 \tau > t_1 \quad (13)$$

where λ is related to the shear rate for the pipe flow and τ is an integral time scale. Using Lumley's definitions of λ and τ for pipe flow we obtain,

$$T_1 \frac{U_*^2}{\nu} > 3 \quad (14)$$

When eq. 9 is put in terms of T_1 ,

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$$\delta p - \delta w = \frac{(\text{Const})C}{\sqrt{2\pi} \beta} \int_0^\infty e^{\frac{-(\ln T_1)^{0.562} - m - \text{Const.})^2}{2\beta^2}} \frac{dT_1}{T_1^{0.562}} \quad (15)$$

which is like a cumulative distribution function for the timescale.

In another form eq. 15 is

$$\delta p - \delta w = \frac{1.03 \times 10^{-4} C \langle M \rangle^{0.78}}{\sqrt{2\pi}} e^{-0.0858\beta^2} \int_X^\infty e^{-z^2/2} dz, \quad (16)$$

$$X = \frac{\ln M_0 - m - 0.78\beta^2}{\beta}$$

Here M_0 can be related to U_*^2/ν . This equation applies only when the behavior is between that for water and maximum drag reduction. Also the proportionality factor should be a function of Reynolds number, U_*D/ν . Then it would be best to use Δ_g as a characterization factor, since a ratio would eliminate the Reynolds number dependence.

$$\Delta_s = \frac{\delta_p - \delta_w}{\delta_M - \delta_w} = \frac{C_p \langle M_p \rangle^{0.78} e^{-0.0858 \beta_p^2} \int_{X_p}^{\infty} e^{-z^2/2} dz}{C_M \langle M_M \rangle^{0.78} e^{-0.0858 \beta_M^2} \int_{X_M}^{\infty} e^{-z^2/2} dz}, \quad (17)$$

is a possible ratio where the denominator refers to maximum drag reduction. Unfortunately this requires a standard of comparison for each $U_* D/\nu$. One standard which can be deduced from previous data is the limit when X_M is negative infinity.

Consider

$$\frac{\delta_M - \delta_w}{KC_M \langle M_M \rangle^{0.78} e^{-0.0858 \beta_M^2}} = \frac{1}{\sqrt{2\pi}} \int_{X_M}^{\infty} e^{-z^2/2} dz \quad (18)$$

where K is the proportionality factor. In Patterson and Abernathy (1970), $\langle M^2 \rangle / \langle M \rangle^2$ was found to be approximately 20 for the Polyox WSR series. This gives $\beta = 1.73$ and since $\langle M^2 \rangle / \langle M \rangle$, the weight average molecular weight is 8×10^6 we can also get $\langle M \rangle$. Then for points between the water and maximum drag reduction curves we can find X_M corresponding to the proper fraction of $\delta_M - \delta_w$. For such a wide distribution we can assume that the effects of the distribution

will far outweigh any Reynolds number dependence. We will assume this fraction applies to the flowrate at constant U_*^2/ν . For Patterson and Abernathy's data

Fraction of ($\delta_M - \delta_w$)	X	M_o	T_1	U_*^2/ν
0.01	2.326	5.7×10^7	1.33×10^{-1}	2.25×10
0.10	1.282	8.5×10^6	4.5×10^{-3}	6.6×10^2
0.25	.674	2.97×10^6	6.6×10^{-4}	4.5×10^3
0.50	0	9.2×10^5	8.3×10^{-5}	3.6×10^4
0.75	- .674	2.85×10^5	1.04×10^{-5}	2.94×10^5
0.90	-1.282	1×10^5	1.53×10^{-6}	1.98×10^6
0.99	-2.326	1.49×10^4	5.2×10^{-8}	5.7×10^7

These points are plotted on fig. 3 and in terms of Reynolds number vs. friction factor on fig. 4. The concentration corresponding to this curve is approximately 4 ppm by weight on fig. 4. Similar curves for other concentrations can be prepared by multiplying the fraction of ($\delta_M - \delta_w$) in the table by $C/4$ where C is the concentration in parts per million. Curves for various multiples of the minimum curve are also shown on fig. 3 and 4 and compared with experimental data on fig. 4. When concentrations are much less or much more than the minimum to reach maximum drag reduction, the agreement is only fair since the log normal distribution is only an approximation.

However, the result qualitatively describes the behavior quite well especially if the straight line portions of the curves on fig. 3 are extrapolated to the water and maximum drag reduction curves. We see that many observations on dilute polymer solutions are merely due to the molecular weight distribution.

To interpret the Polyometer curves we see that the onset point, slope of the curve between onset and maximum drag reduction and the intersection point with the maximum drag reduction line are functions of concentration, average molecular weight and the parameter β related to the ratio of weight average to number average molecular weight. It would be easier to relate the intersection point with the maximum drag line with the appropriate fresh Polyox WSR 301 since the exact nature of the degradation is unknown. Another possibility is to use the appropriate shear rate for the test and relate this to curves like those on fig. 3. As we can see on fig. 3 the curves depend on the pipe size.

Fig. 5 and 6 show the correlation of maximum drag reduction intercept with concentration of fresh Polyox WSR 301. Using fig. 6 for the 48-inch tunnel test we obtain the following for a speed of 8.5 meters per second

Test	Equivalent Fresh Concentration
7627	> 10
7629	10
7632	7
7633	5
7635	3
7639	1.8
7641	2.5

This equivalent would be different for each speed since the onset point is not equivalent to the original Polyox. For example text 7633 corresponds to an onset shear rate of $4 \times 10^3 \text{ sec}^{-1}$. On fig. 5 the onset point is plotted for this range and at $4 \times 10^3 \text{ sec}$ we obtain 1.5 ppm compared to 5 ppm from the comparison at a shear rate of $8 \times 10^4 \text{ sec}^{-1}$. Obviously the concentration is greater than any of these based on fresh Polyox WSR 301 but the molecular weight average is less. We can estimate the average molecular weight and concentration if we assume β is unchanged. This is reasonable only because β is quite large anyway and the probable increase in the weight average to number average molecular weight ratio would not change β by much. Let us further assume that the concentration remains constant so only molecular weight changes and plot the results on fig. 7. The minimum

concentration to reach maximum drag reduction for various weight average molecular weights is found to be as follows:

M_w	Minimum Concentration for Maximum Drag Reduction
8×10^6	4 ppm
4×10^6	6.9 ppm
2×10^6	11.7 ppm
1×10^6	20.3 ppm
5×10^5	34.7 ppm

The log normal model predicts minimum concentrations to reach maximum drag reduction in agreement with Patterson and Abernathy. In addition the apparent "onset" shear rate increases with decreasing average molecular weight and decreases with concentration increase also in agreement with their data. We also find the same behavior in stretching out the curves when the "onset" is within the laminar flow regime for the pipe used as shown on fig. 3. Much of the "unusual" behavior of the polymer solutions are therefore only a result of the molecular weight distribution. Fig. 7 can be used to estimate the weight average molecular weight for the 48-inch tunnel test.

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The approximate results are as follows:

Test	M_w
7627	8×10^6
7629	3×10^6
7632	2×10^6
7633	1.5×10^6
7635	1×10^6
7639	0.7×10^6
7641	0.9×10^6

Effects other than drag reduction are found for increased concentrations for fresh solutions and are not included in this analysis.

We can see from this analysis that a polymer ocean test can be characterized by the equivalent of fresh polymer or the average molecular weight. Either of these can be estimated as described herein. In a separate attachment to this report a "cookbook" method for preparing these estimates is given.

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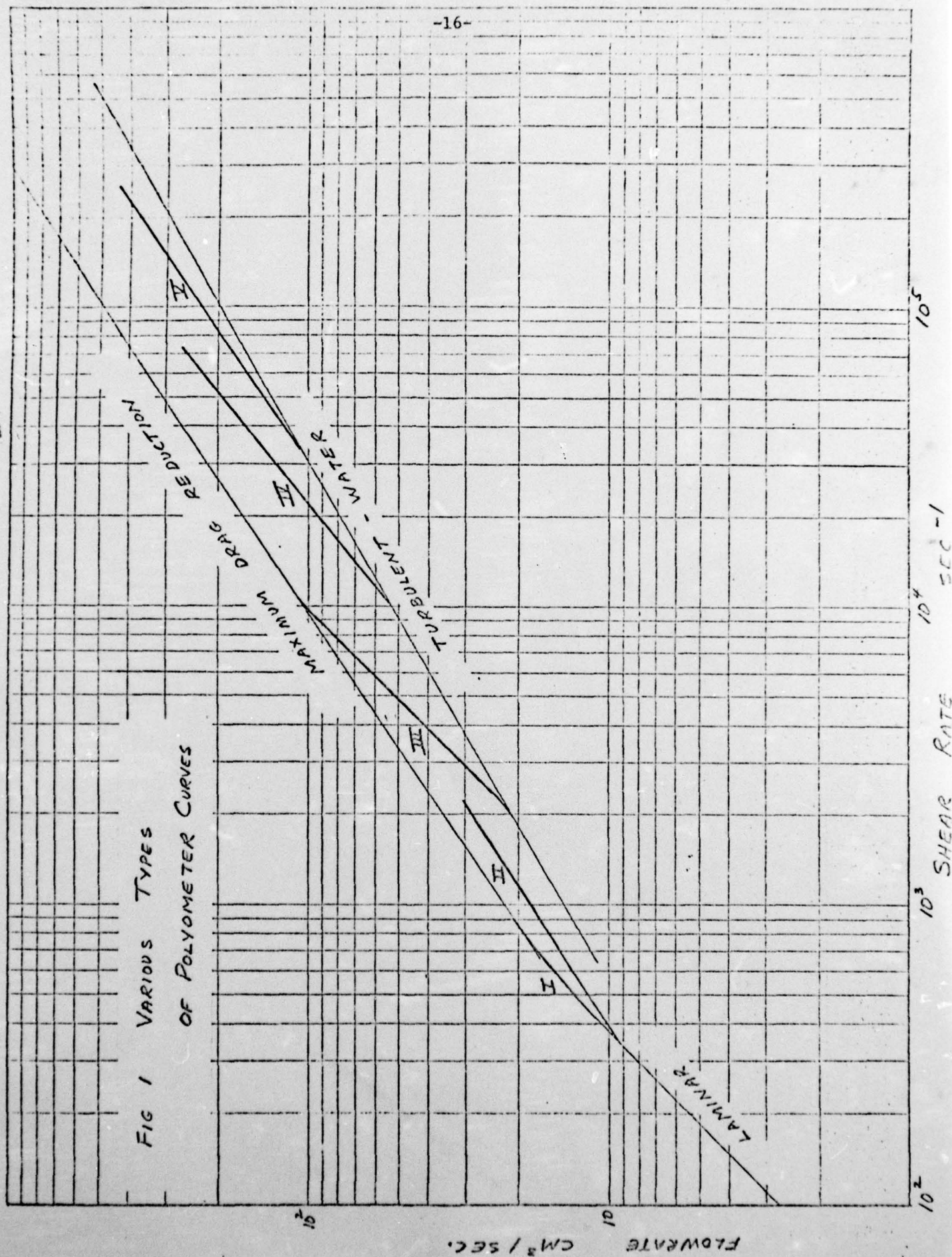


FIG 1 VARIOUS TYPES OF POLYOMETER CURVES

1-2.35 $\frac{1}{\sqrt{2}} = 10^4$ SEC RATE = 10^3 501

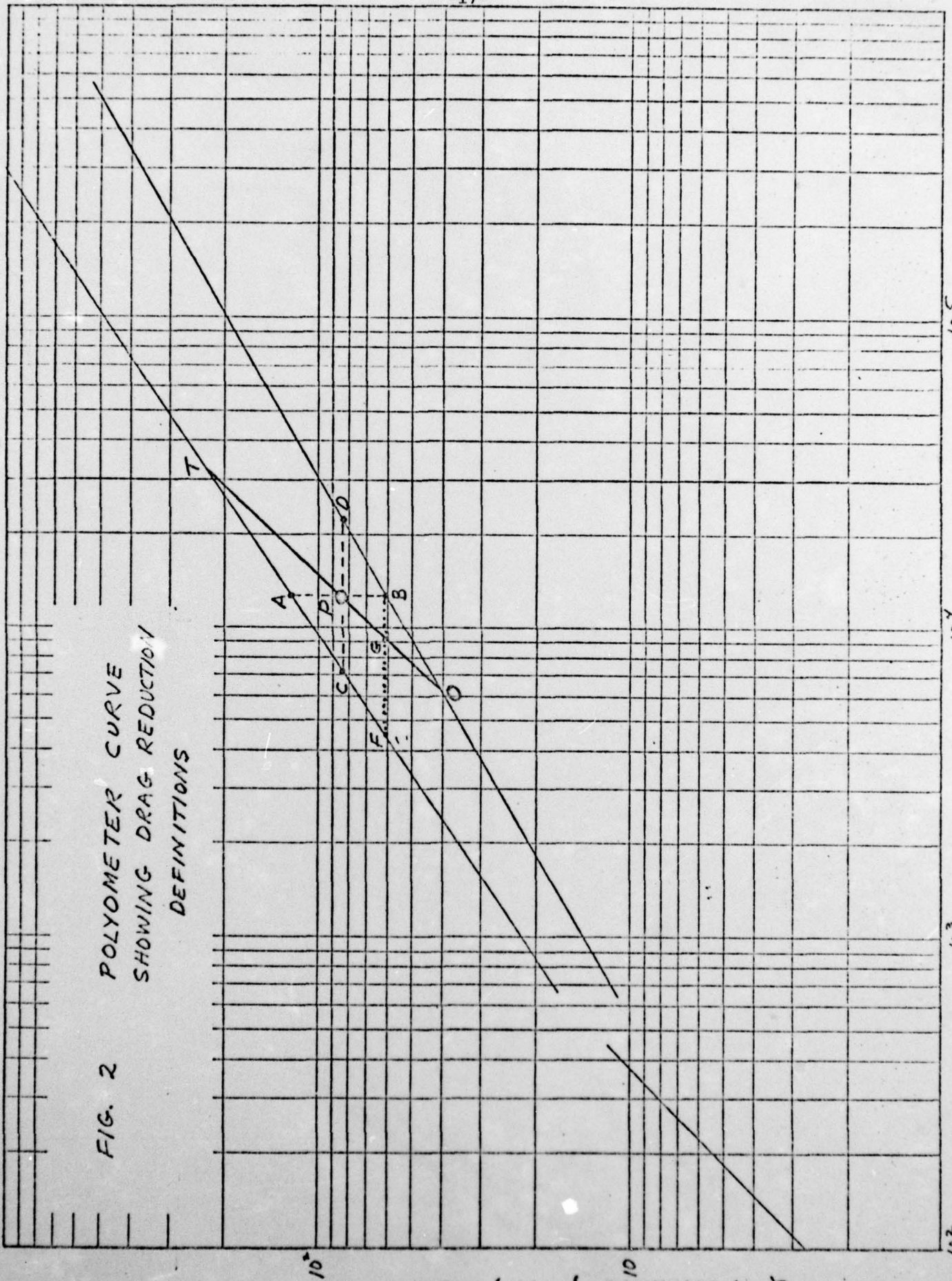
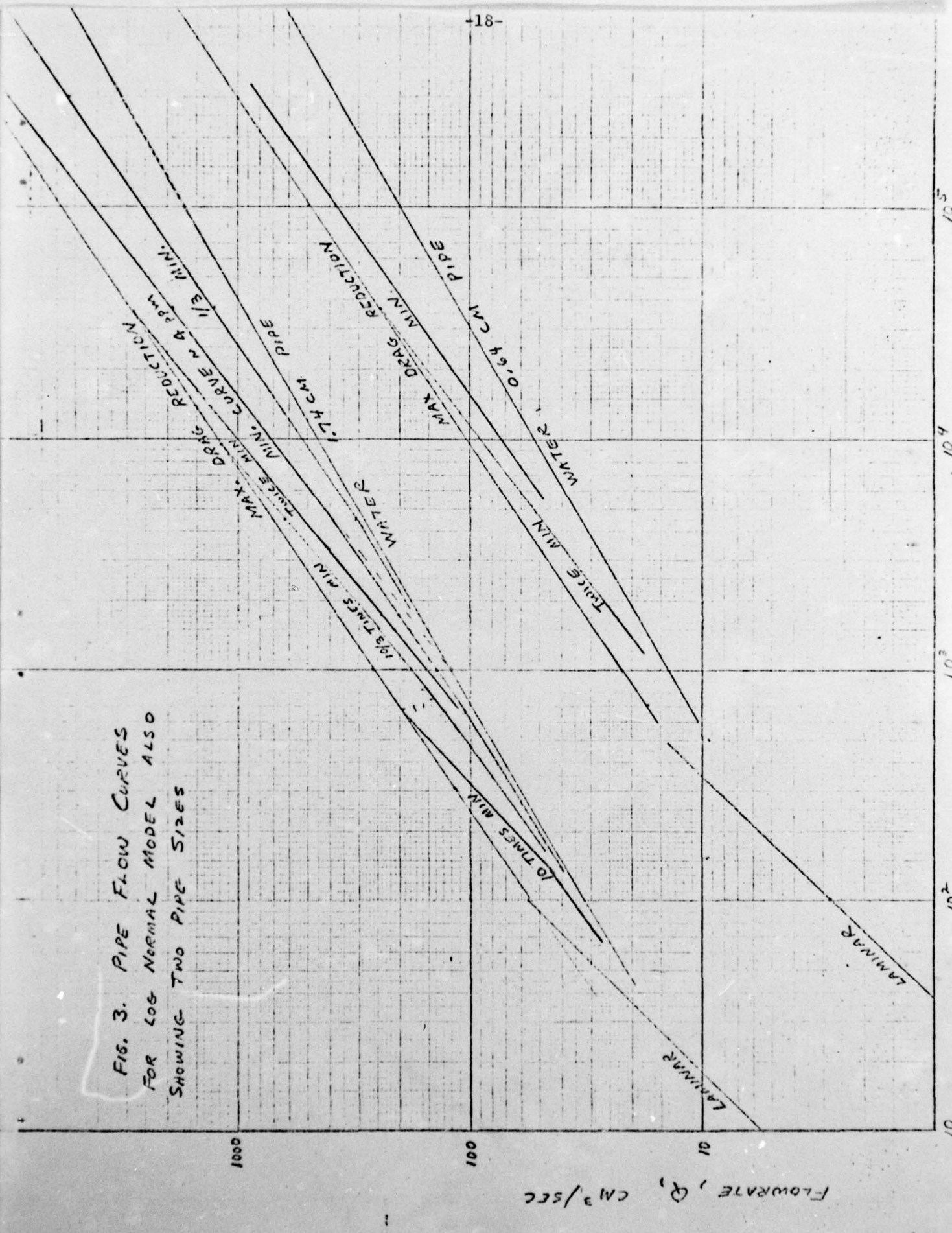


FIG. 3. PIPE FLOW CURVES
FOR LOS NORMAL MODEL ALSO
SHOWING TWO PIPE SIZES



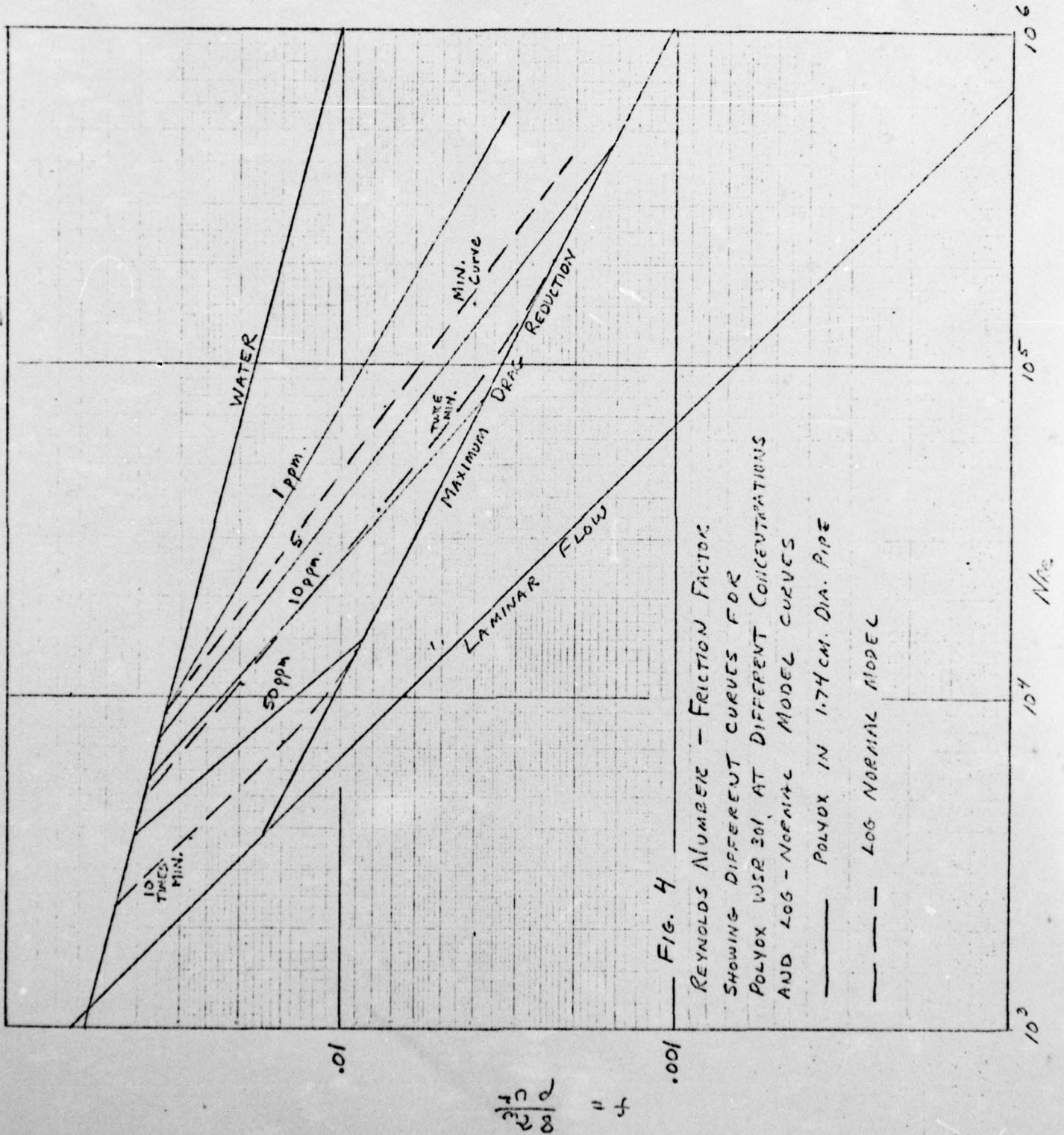
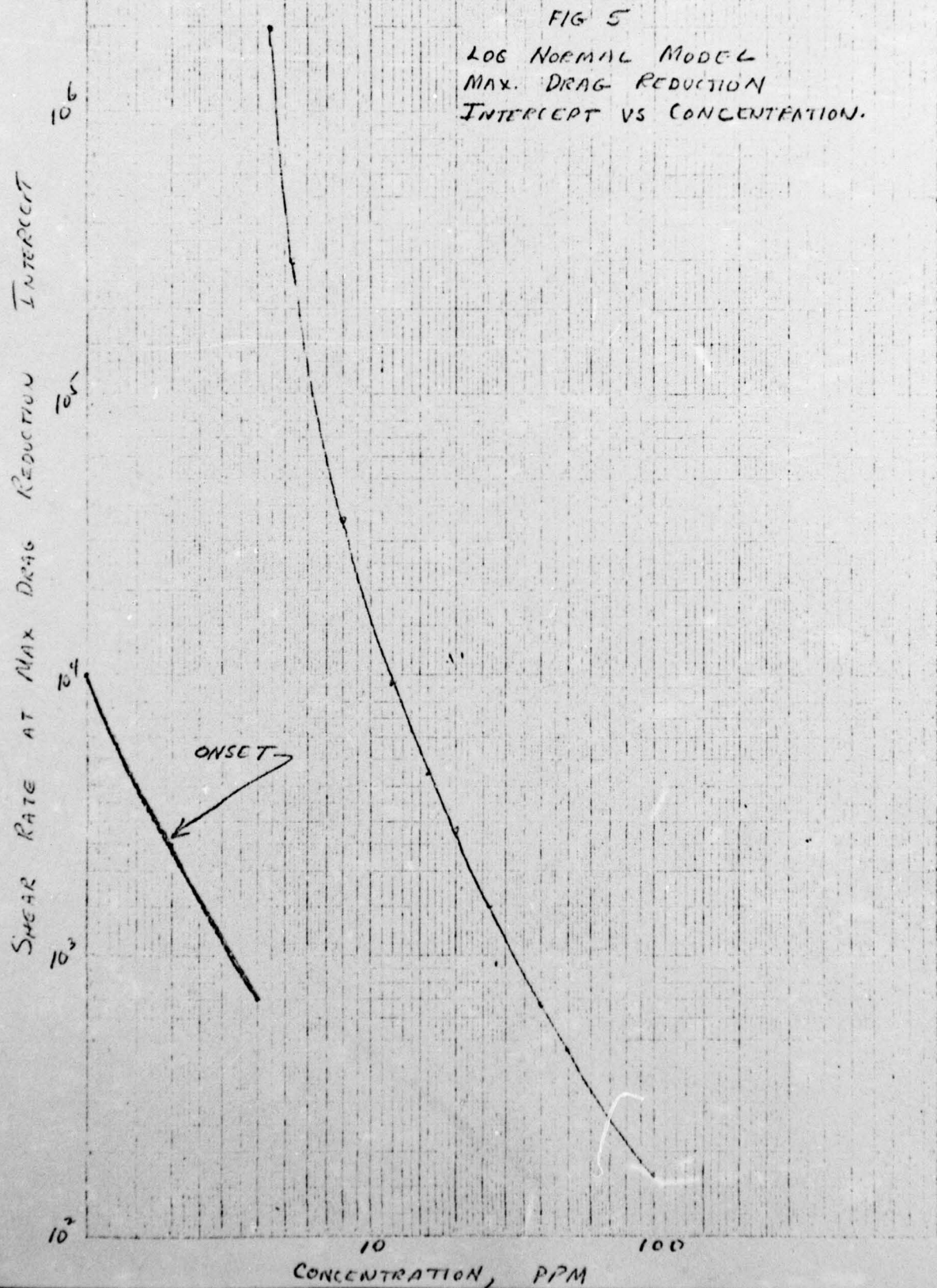


FIG. 4
REYNOLDS NUMBER - FRICTION FACTOR
SHOWING DIFFERENT CURVES FOR
POLYOX WSR 301 AT DIFFERENT CONCENTRATIONS
AND LOG-NORMAL MODEL CURVES
POLYOX IN 1.74 CM. DIA. PIPE
LOG-NORMAL MODEL

$$\frac{31}{8} \approx 4$$



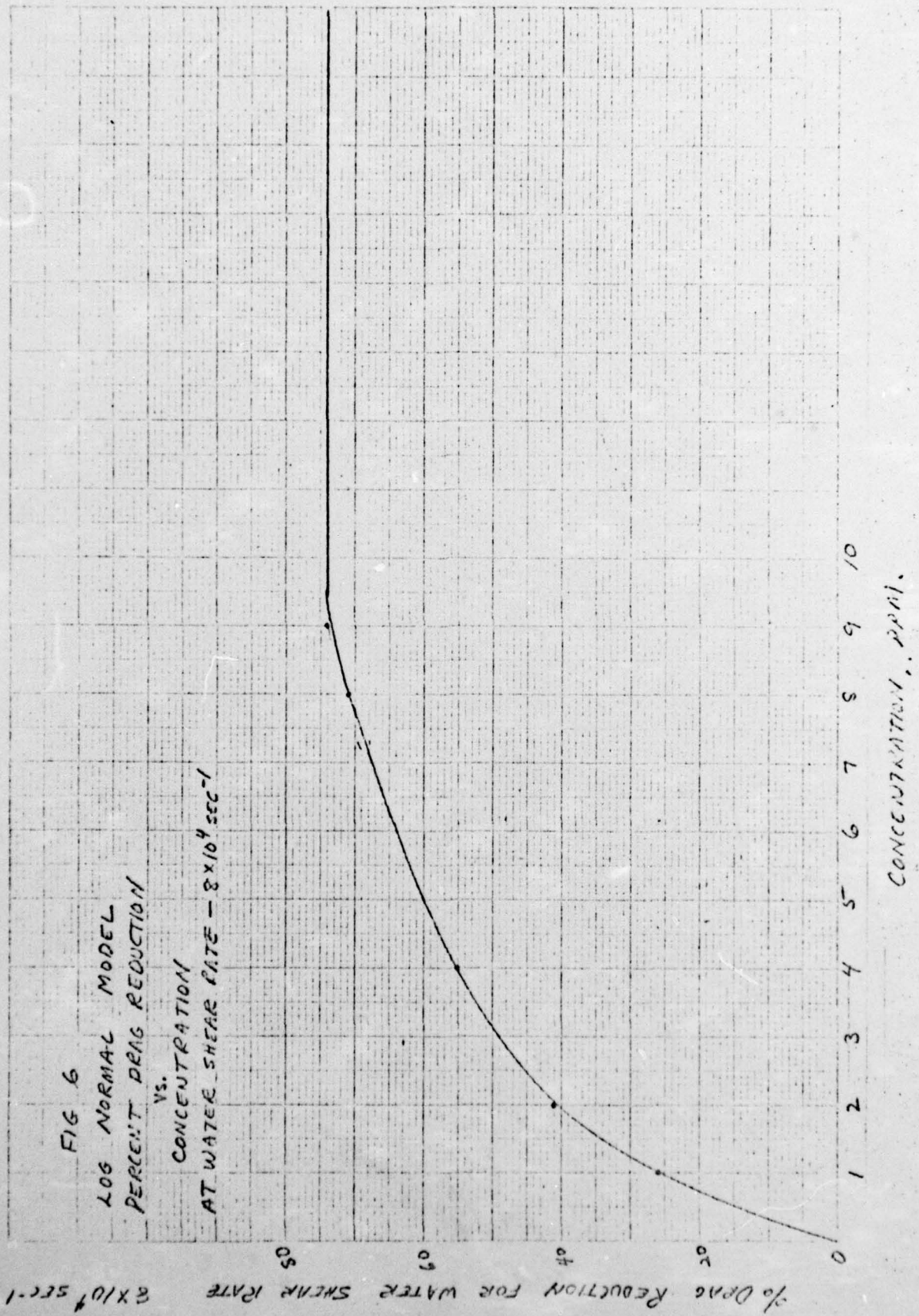
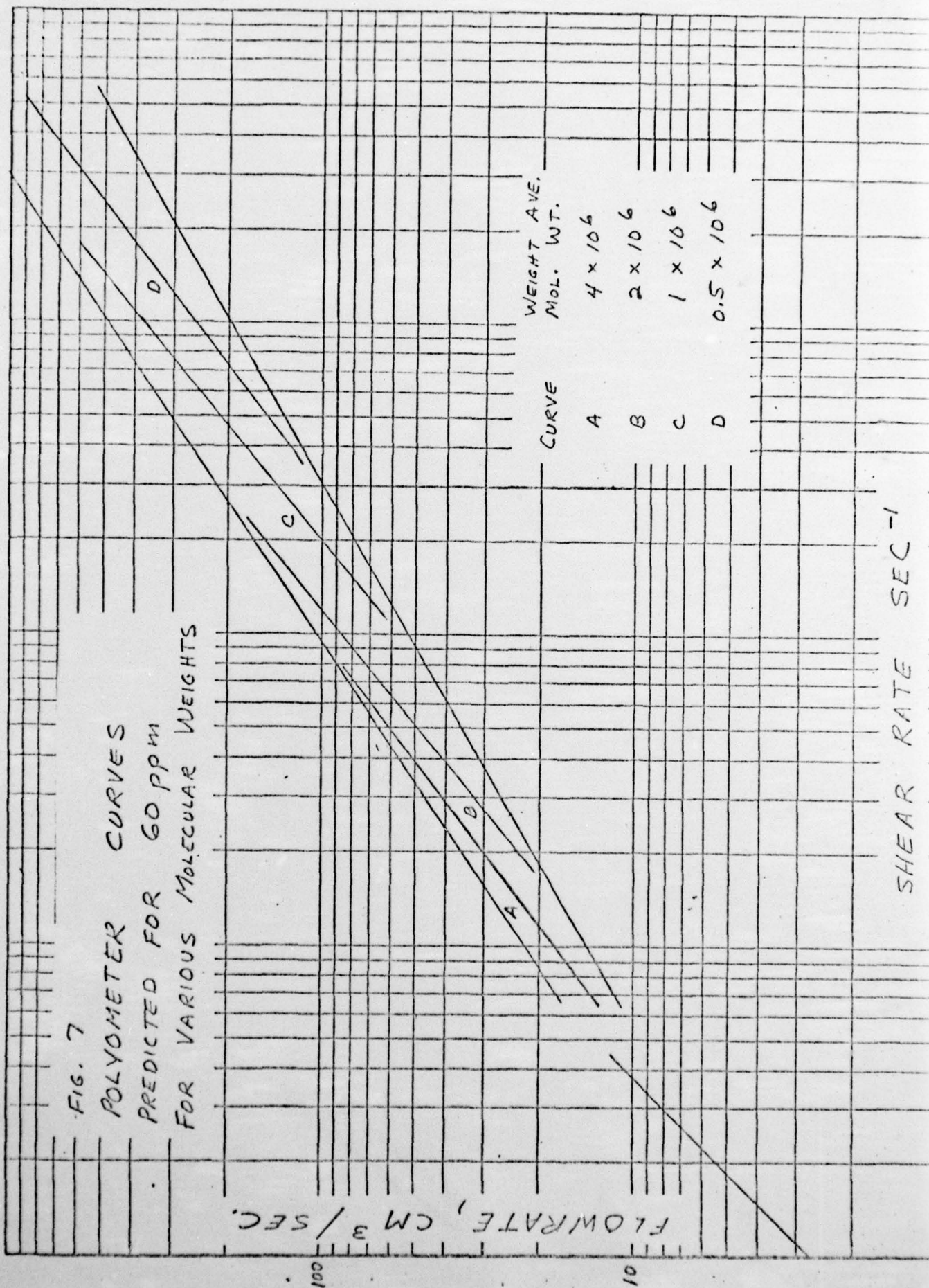


FIG. 7
POLYMER CURVES
PREDICTED FOR 60 ppm
FOR VARIOUS MOLECULAR WEIGHTS



Preparation of Polyometer Curves from Log Normal Model

We assume that for Polyox WSR 301 the weight average molecular weight is 8×10^6 , the ratio of weight average to number average molecular weight is 20 and the minimum concentration to reach maximum drag reduction line is 4 ppm. Points on the master curve are as follows:

fraction = f1	X	Shear-rate, sec ⁻¹ = U_*^2/ν
.99	-2.326	5.7×10^7
.90	-1.282	1.98×10^6
.75	-.674	2.94×10^5
.50	0	3.6×10^4
.333	+.432	9.5×10^3
.25	.674	4.5×10^3
.20	.842	2.73×10^3
.15	1.036	1.5×10^3
.10	1.282	6.9×10^2
.08	1.405	4.6×10^2
.06	1.555	3.05×10^2
.04	1.751	1.63×10^2
.02	2.054	6.4×10
.01	2.326	2.75×10

Case I - No degradation only concentration is changed.

- a. Multiply the numbers in the fraction column by the concentration in ppm divided by 4. Disregard all numbers greater than 1.

- b. Plot the resulting fraction and corresponding shear rate.

At the constant shear rate, read the flow rates for

water, Q_w , and maximum drag reduction, Q_M . Calculate Q_p

$$Q_p = Q_w + f1 (Q_p - Q_w).$$

Plot Q_p at the shear rate.

- c. When sufficient points have been located, draw a straight line through the points in the central region between the water and maximum drag reduction curves and extrapolate the line to these two curves. Disregard the points not on this line.

Case II - Typical polymer ocean test, concentration is constant but molecular weight is changed.

- a. Calculate the ratio 8×10^6 to the weight average molecular weight of the curve to be plotted. Calculate the following:

$$S \equiv (8 \times 10^6 / M_w)^{0.78}$$

$$W \equiv (8 \times 10^6 / M_w)^{1.78}$$

- b. The new minimum concentration to reach maximum drag reduction is $4S$. The fraction numbers are multiplied by concentration divided by $4S$ and the shear rate numbers are multiplied by W . Form a new table.
- c. Proceed as in case I, b and c.

Case III. The ratio of weight average to number average molecular weight is changed.

a. Find β where

$$\beta = \sqrt{\ln (\text{wt. ave./no. ave.})}$$

b. The U_*^2/v is found from β , X , and the weight average molecular weight.

$$\frac{U_*^2}{v} = \frac{3 \times 10^{15} e^{1.29\beta^2}}{2 M_w^{1.78} e^{1.78\beta X}}$$

c. The new minimum concentration to reach maximum drag reduction is found from β and the weight average molecular weight.

$$C_{\text{Min}} = .03 \left(\frac{8 \times 10^6}{M_w} \right)^{0.78} e^{+1.638\beta^2}$$

d. Proceed to case I or II for the change in concentration from C_{Min} and U_*^2/v generated.

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